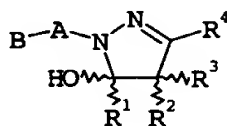


532 Rec'd PCT/PTO 02 APR 2001

Use of substituted 5-hydroxypyrazoles, novel 5-hydroxypyrazoles, processes for their preparation and compositions comprising them

5 The present invention relates to the use of 5-hydroxypyrazolines of the formula I



I

10

where:

15 B is aryl with or without substitution or hetaryl with or without substitution;

A is C=O, C=S or SO₂;

20 R¹ is C₂-C₁₀-alkyl, C₁-C₁₀-haloalkyl, C₃-C₁₀-alkenyl, C₃-C₁₀-haloalkenyl, C₃-C₁₀-alkynyl or C₃-C₁₀-haloalkynyl,

C₃-C₁₀-cycloalkyl with or without substitution, C₃-C₁₀-cycloalkenyl with or without substitution, C₃-C₁₀-cycloalkynyl with or without substitution or,

25

aryl with or without substitution, heterocyclyl with or without substitution or hetaryl with or without substitution;

30 R² is hydrogen;

30

R³ is hydrogen, nitro, cyano, N(R')₂, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₂-C₄-alkenyl, C₂-C₄-haloalkenyl, C₂-C₄-alkynyl or C₂-C₄-haloalkynyl, where

35 R' independently of one another are hydrogen or C₁-C₄-alkyl;

or R² and R³ together are a group

=O, =S or =N-O-R⁵, where

40

R⁵ is hydrogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₃-C₆-alkenyl, C₃-C₆-haloalkenyl, C₃-C₆-alkynyl or C₃-C₆-haloalkynyl;

45 R⁴ is hydrogen, halogen, nitro, cyano, N(R')₂, C₁-C₄-alkyl, C₁-C₄-haloalkyl, COOR', hetaryl or heterocyclyl;

for controlling harmful fungi, and compositions comprising them.

Furthermore, the invention relates to novel 5-hydroxypyrazoles and to processes for their preparation.

5

Substituted pyrazolin-5-ones having herbicidal and fungicidal activity are known from DE-A 37 28 278, and fungicidally active 3-arylpyrazoles are disclosed in WO-A 94/29276.

10 However, their activity is in many instances unsatisfactory.

It is an object of the present invention to provide compounds having improved activity.

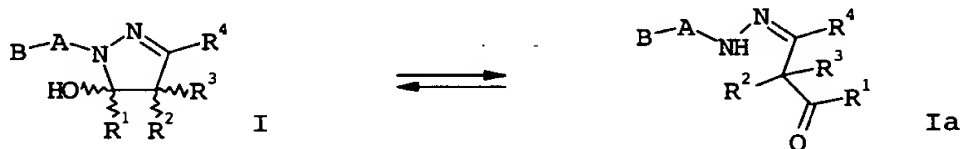
15 We have found that this object is achieved by the use of substituted 5-hydroxypyrazoles of the formula I as fungicide, and by compositions comprising them.

Individual 1-benzoyl-5-hydroxypyrazolines are known from Acta
 20 Chem. Scand., 24 (1970), 1744; Zh. Org. Khim., 15 (1979), 1100; ibid. 16 (1980), 415 and 2235; ibid. 17 (1981), 284; ibid. 18 (1982), 762; ibid. 20 (1984), 1371; ibid. 21 (1985), 2493; ibid. 22 (1986), 286 and 2043; ibid. 23 (1987), 1433; Khim. Geterotski Soedin 9 (1987), 1210; Indian J. Chem. Sect.B, 29B (1990), 887;
 25 Inorg. Chem. 31 (1992), 598; J. Fluorine Chem. 65 (1993), 21 and Tetrahedron 50 (1994), 11447. However, the biological activity of these compounds is not known in the prior art.

Compounds of the formula I are present in a tautomeric
 30 equilibrium with the open-chain form Ia [cf.: J. Org. Chem. USSR (1983), 2037; ibid. (1984), 1247].

The invention therefore relates to both forms, even if, for the sake of clarity, only the ring form I is mentioned in each case.

35

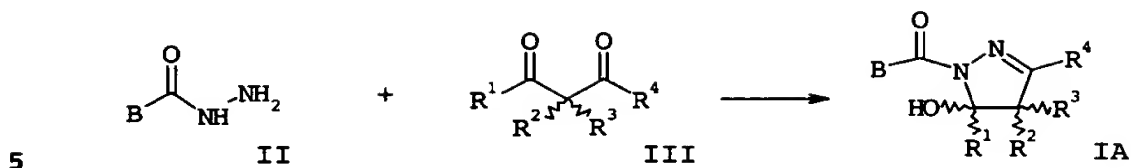


40

Compounds of the formula I in which A is C=O (formula IA) can be obtained, for example, by the following route:

45

3



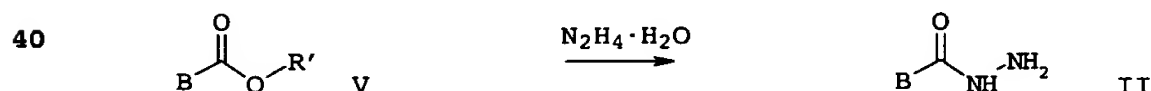
This reaction is usually carried out at from 0°C to 200°C, preferably from 20°C to 100°C, in an inert organic solvent [J. Org. Chem. USSR (Engl. Transl.), 16 (1980), 371; *ibid.* 21 (1985), 2279; *ibid.* 22 (1986), 250; *ibid.* 23 (1987), 1291; Indian J. Chem. Sect. B, 29 (1990), 887; Bull. Soc. Chem. Jp. 62 (1989), 3409].

Suitable solvents are aliphatic hydrocarbons, aromatic hydrocarbons, such as toluene, o-, m- and p-xylene, halogenated hydrocarbons, such as methylene chloride, chloroform and chlorobenzene, ethers, such as diethyl ether, diisopropyl ether, tert-butyl methyl ether, dioxane and tetrahydrofuran, nitriles, such as acetonitrile and propionitrile, alcohols, such as methanol, ethanol, n-propanol, isopropanol, n-butanol and tert-butanol, and also dimethyl sulfoxide, dimethylformamide and dimethylacetamide, particularly preferably methanol, ethanol and tetrahydrofuran. It is also possible to use mixtures of the abovementioned solvents.

The starting materials are generally reacted with one another in equimolar amounts. In terms of yield, it may be advantageous to employ an excess of III, based on II.

The hydrazides of the formula II required for preparing the compounds I are known from the literature [cf. J. Heterocycl. Chem. 16 (1976), 561; Helv. Chim. Acta, 27 (1944), 883; J. Chem. Soc. (1943), 413], or they can be prepared in accordance with the literature cited.

Hydrazides of the formula II are usually prepared from the corresponding carboxylic esters of the formula V by reaction with hydrazine hydrate. In the formula V, R' is C₁-C₄-alkyl.

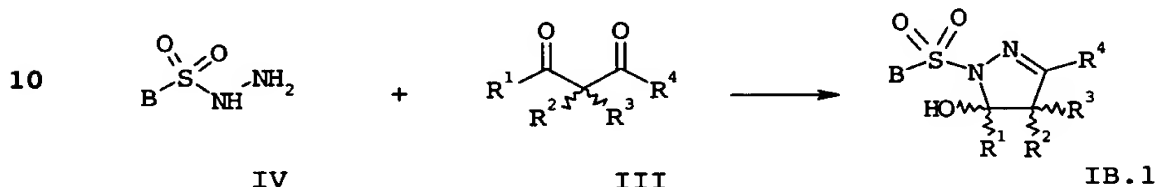


This reaction is usually carried out at from 0°C to 150°C, preferably from 20°C to 100°C, in an inert organic solvent [cf. J. Heterocycl. Chem. 16 (1976), 561; Helv. Chim. Acta, 27 (1944), 883; J. Chem. Soc. (1943), 413].

The diketones of the formula III required for preparing the compounds I are also known from the literature [Organikum, VEB Verlag der Wissenschaften, 15th ed. p. 584ff., Berlin 1976], or they can be prepared in accordance with the literature cited.

5

Compounds of the formula I in which A is SO₂ (formula IB.1) are preferably obtainable by the following route:



This reaction is advantageously carried out under the conditions 15 given for preparing the compounds IA.

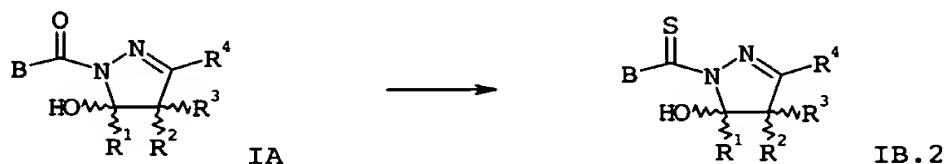
The starting materials are generally reacted with one another in equimolar amounts. In terms of yield, it may be advantageous to employ an excess of III, based on IV.

20

The sulfohydrazides of the formula IV required for preparing the compounds I are known from the literature [J. Chem. Soc. Chem. Commun. (1972), 1132; J. Chem. Soc. (1949), 1148; Helv. Chim. Acta, 42.(1962), 996], or they can be prepared in accordance with 25 the literature cited.

The compounds of the formula I in which A is C=S (formula IB.2) are obtainable from the corresponding compounds of the formula IA by reaction with a sulfurizing agent.

30



35

The sulfurization of IA is carried out under conditions known per se, usually at from 0°C to 180°C, preferably from 20°C to 140°C, in an inert organic solvent [cf. Liebigs Ann. Chem., (1989), 177].

40

Suitable solvents are aliphatic hydrocarbons, such as pentane, hexane, cyclohexane and petroleum ether, aromatic hydrocarbons, such as toluene, o-, m- and p-xylene, halogenated hydrocarbons, such as methylene chloride, chloroform and chlorobenzene, ethers, 45 such as diethyl ether, diisopropyl ether, tert-butyl methyl ether, dioxane, anisole and tetrahydrofuran, nitriles, such as acetonitrile and propionitrile, and also dimethyl sulfoxide,

particularly preferably toluene and tetrahydrofuran. It is also possible to employ mixtures of the abovementioned solvents.

Suitable sulfurizing agents are, for example, phosphorus pentasulfide or Lawesson's reagent.

The reaction mixtures are worked up in a customary manner, for example by mixing with water, phase separation and, if required, chromatographic purification of the crude products. Some of the intermediates and end products are obtained in the form of colorless or slightly brownish, viscous oils, which are purified or freed from volatile components under reduced pressure and at moderately elevated temperatures. If the intermediates and end products are obtained as solids, purification can also be carried out by recrystallization or digestion.

In the definitions of the symbols given in the above formulae, collective terms were used which generally represent the following substituents:

20

Halogen: fluorine, chlorine, bromine and iodine;

Alkyl: saturated, straight-chain or branched hydrocarbon radicals having 1 to 4, 6, 8 or 10 carbon atoms, for example C₁-C₆-alkyl such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;

35

Haloalkyl: straight-chain or branched alkyl groups having 1 to 10 carbon atoms (as mentioned above), where the hydrogen atoms in these groups may be partially or fully replaced by halogen atoms as mentioned above, for example C₁-C₂-haloalkyl such as chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-chloroethyl, 1-bromoethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl and pentafluoroethyl;

Alkoxy: straight-chain or branched alkyl groups having 1 to 10 carbon atoms (as mentioned above) which are linked to the skeleton via an oxygen atom (-O-);

- 5 **Haloalkoxy:** straight-chain or branched haloalkyl groups having 1 to 10 carbon atoms (as mentioned above) which are linked to the skeleton via an oxygen atom (-O-);

- 10 **Alkylthio:** straight-chain or branched alkyl groups having 1 to 10 or 1 to 4 carbon atoms (as mentioned above) which are linked to the skeleton via a sulfur atom (-S-);

- 15 **Alkylamino:** a straight-chain or branched alkyl group having 1 to 10 carbon atoms (as mentioned above) which is linked to the skeleton via an amino group (-NH-);

- 20 **Dialkylamino:** two straight-chain or branched alkyl groups having in each case 1 to 10 carbon atoms (as mentioned above) which are independent of each other and which are linked to the skeleton via a nitrogen atom;

- 25 **Alkylcarbonyl:** a straight-chain or branched alkyl group having 1 to 10 carbon atoms (as mentioned above), which is linked to the skeleton via a carbonyl group (-CO-);

- Alkoxy carbonyl:** an alkoxy group having 1 to 10 carbon atoms (as mentioned above) which is linked to the skeleton via a carbonyl group (-CO-);

- 30 **Alkylthiocarbonyl:** an alkylthio group having 1 to 10 carbon atoms (as mentioned above) which is linked to the skeleton via a carbonyl group (-CO-);

- 35 **Alkylsulfonyl:** a straight-chain or branched alkyl group having 1 to 10 carbon atoms (as mentioned above), which is linked to the skeleton via a sulfonyl group (-SO₂-);

- 40 **Dialkylaminosulfonyl:** a dialkylamino group (as mentioned above) which is linked to the skeleton via a sulfonyl group (-SO₂-);

- Alkenyl:** unsaturated, straight-chain or branched hydrocarbon radicals having 2 to 4, 6, 8 or 10 carbon atoms and a double bond in any position, for example C₂-C₆-alkenyl such as ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl,

- 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl,
 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl,
 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-
 1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, 1-ethyl-
 5 2-propenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl,
 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-
 1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-
 2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-
 3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-
 10 3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-
 4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl,
 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-
 2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl,
 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, 2,2-dimethyl-
 15 3-butenyl, 2,3-dimethyl-1-butenyl, 2,3-dimethyl-2-butenyl,
 2,3-dimethyl-3-butenyl, 3,3-dimethyl-1-butenyl, 3,3-dimethyl-
 2-butenyl, 1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-
 3-butenyl, 2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2-ethyl-
 3-butenyl, 1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-
 20 2-propenyl, 1-ethyl-2-methyl-1-propenyl and 1-ethyl-2-methyl-
 2-propenyl;

Haloalkenyl: unsaturated, straight-chain or branched hydrocarbon
 radicals having 2 to 10 carbon atoms and a double bond in any
 25 position (as mentioned above), where the hydrogen atoms in these
 groups may be partially or fully replaced by halogen atoms as
 mentioned above, in particular by fluorine, chlorine and bromine;

Alkenyloxy: unsaturated, straight-chain or branched hydrocarbon
 30 radicals having 3 to 10 carbon atoms and a double bond in any
 position which is not adjacent to the hetero atom (as mentioned
 above) which are linked to the skeleton via an oxygen atom (-O-);

Alkenylcarbonyl: unsaturated, straight-chain or branched
 35 hydrocarbon radicals having 2 to 10 carbon atoms and a double
 bond in any position (as mentioned above) which are linked to the
 skeleton via a carbonyl group (-CO-);

Alkynyl: straight-chain or branched hydrocarbon groups having 2
 40 to 4, 6, 8 or 10 carbon atoms and a triple bond in any position,
 for example C₂-C₆-alkynyl such as ethynyl, 1-propynyl, 2-propynyl,
 1-butyne, 2-butyne, 3-butyne, 1-methyl-2-propynyl, 1-pentyne,
 2-pentyne, 3-pentyne, 4-pentyne, 1-methyl-2-butyne, 1-methyl-
 3-butyne, 2-methyl-3-butyne, 3-methyl-1-butyne, 1,1-dimethyl-
 45 2-propynyl, 1-ethyl-2-propynyl, 1-hexynyl, 2-hexynyl, 3-hexynyl,
 4-hexynyl, 5-hexynyl, 1-methyl-2-pentyne, 1-methyl-3-pentyne,
 1-methyl-4-pentyne, 2-methyl-3-pentyne, 2-methyl-4-pentyne,

3-methyl-1-pentynyl, 3-methyl-4-pentynyl, 4-methyl-1-pentynyl,
 4-methyl-2-pentynyl, 1,1-dimethyl-2-butynyl, 1,1-dimethyl-
 3-butynyl, 1,2-dimethyl-3-butynyl, 2,2-dimethyl-3-butynyl,
 3,3-dimethyl-1-butynyl, 1-ethyl-2-butynyl, 1-ethyl-3-butynyl,
 5 2-ethyl-3-butynyl and 1-ethyl-1-methyl-2-propynyl;

Haloalkynyl: unsaturated, straight-chain or branched hydrocarbon
 radicals having 2 to 10 carbon atoms and a triple bond in any
 position (as mentioned above), where the hydrogen atoms in these
 10 groups may be partially or fully replaced by halogen atoms as
 mentioned above, in particular fluorine, chlorine and bromine;

Cycloalkyl: monocyclic, saturated hydrocarbon groups having 3 to
 6, 8, 10 or 12 carbon ring members, for example C₃-C₈-cycloalkyl
 such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl,
 15 cycloheptyl and cyclooctyl;

Cycloalkoxy: monocyclic, saturated hydrocarbon groups having 3 to
 12 carbon ring members (as mentioned above), which are linked to
 the skeleton via an oxygen atom (-O-);

20 **Cycloalkylamino:** monocyclic, saturated hydrocarbon groups having
 3 to 12 carbon ring members (as mentioned above) which are linked
 to the skeleton via an amino group (-NH-);

25 **Heterocyclyl:** 5- or 6-membered heterocycles containing, in
 addition to carbon ring members, one to three nitrogen atoms
 and/or one oxygen or sulfur atom or one or two oxygen and/or
 sulfur atoms, for example 2-tetrahydrofuranyl,
 3-tetrahydrofuranyl, 2-tetrahydrothienyl, 3-tetrahydrothienyl,
 30 2-pyrrolidinyl, 3-pyrrolidinyl, 3-isoxazolidinyl,
 4-isoxazolidinyl, 5-isoxazolidinyl, 3-isothiazolidinyl,
 4-isothiazolidinyl, 5-isothiazolidinyl, 3-pyrazolidinyl,
 4-pyrazolidinyl, 5-pyrazolidinyl, 2-oxazolidinyl, 4-oxazolidinyl,
 5-oxazolidinyl, 2-thiazolidinyl, 4-thiazolidinyl,
 35 5-thiazolidinyl, 2-imidazolidinyl, 4-imidazolidinyl,
 1,2,4-oxadiazolidin-3-yl, 1,2,4-oxadiazolidin-5-yl,
 1,2,4-thiadiazolidin-3-yl, 1,2,4-thiadiazolidin-5-yl,
 1,2,4-triazolidin-3-yl, 1,3,4-oxadiazolidin-2-yl,
 1,3,4-thiadiazolidin-2-yl, 1,3,4-triazolidin-2-yl,
 40 2,3-dihydrofur-2-yl, 2,3-dihydrofur-3-yl, 2,4-dihydrofur-2-yl,
 2,4-dihydrofur-3-yl, 2,3-dihydrothien-2-yl,
 2,3-dihydrothien-3-yl, 2,4-dihydrothien-2-yl,
 2,4-dihydrothien-3-yl, 2-pyrrolin-2-yl, 2-pyrrolin-3-yl,
 3-pyrrolin-2-yl, 3-pyrrolin-3-yl, 2-isoxazolin-3-yl,
 45 3-isoxazolin-3-yl, 4-isoxazolin-3-yl, 2-isoxazolin-4-yl,
 3-isoxazolin-4-yl, 4-isoxazolin-4-yl, 2-isoxazolin-5-yl,
 3-isoxazolin-5-yl, 4-isoxazolin-5-yl, 2-isothiazolin-3-yl,

- 3-isothiazolin-3-yl, 4-isothiazolin-3-yl, 2-isothiazolin-4-yl,
 3-isothiazolin-4-yl, 4-isothiazolin-4-yl, 2-isothiazolin-5-yl,
 3-isothiazolin-5-yl, 4-isothiazolin-5-yl,
 2,3-dihydropyrazol-1-yl, 2,3-dihydropyrazol-2-yl,
 5 2,3-dihydropyrazol-3-yl, 2,3-dihydropyrazol-4-yl,
 2,3-dihydropyrazol-5-yl, 3,4-dihydropyrazol-1-yl,
 3,4-dihydropyrazol-3-yl, 3,4-dihydropyrazol-4-yl,
 3,4-dihydropyrazol-5-yl, 4,5-dihydropyrazol-1-yl,
 4,5-dihydropyrazol-3-yl, 4,5-dihydropyrazol-4-yl,
 10 4,5-dihydropyrazol-5-yl, 2,3-dihydrooxazol-2-yl,
 2,3-dihydrooxazol-3-yl, 2,3-dihydrooxazol-4-yl,
 2,3-dihydrooxazol-5-yl, 3,4-dihydrooxazol-2-yl,
 3,4-dihydrooxazol-3-yl, 3,4-dihydrooxazol-4-yl,
 3,4-dihydrooxazol-5-yl, 3,4-dihydrooxazol-2-yl,
 15 3,4-dihydrooxazol-3-yl, 3,4-dihydrooxazol-4-yl, 2-piperidinyl,
 3-piperidinyl, 4-piperidinyl, 1,3-dioxan-5-yl,
 2-tetrahydropyranyl, 4-tetrahydropyranyl, 2-tetrahydrothienyl,
 3-hexahydropyridazinyl, 4-hexahydropyridazinyl,
 2-hexahydropyrimidinyl, 4-hexahydropyrimidinyl,
 20 5-hexahydropyrimidinyl, 2-piperazinyl,
 1,3,5-hexahydro-triazin-2-yl and 1,2,4-hexahydrotriazin-3-yl;

Aryl: a mono- to trinuclear aromatic ring system containing 6 to
 14 carbon ring members, for example phenyl, naphthyl and
 25 anthracenyl;

Aryloxy: a mono- to trinuclear aromatic ring system (as mentioned
 above) which is linked to the skeleton via an oxygen atom (-O-);

30 **Arylthio:** a mono- to trinuclear aromatic ring system (as
 mentioned above) which is linked to the skeleton via a sulfur
 atom (-S-);

Arylamino: a mono- to trinuclear aromatic ring system (as
 35 mentioned above) which is linked to the skeleton via an amino
 group (-NH-);

Arylcarbonyl: a mono- to trinuclear aromatic ring system (as
 mentioned above) which is linked to the skeleton via a carbonyl
 40 group (-CO-);

Aryloxycarbonyl: a mono- to trinuclear aryloxy group (as
 mentioned above) which is linked to the skeleton via a carbonyl
 group (-CO-);

45 **Arylthiocarbonyl:** a mono- to trinuclear arylthio group (as
 mentioned above) which is linked to the skeleton via a carbonyl

group (-CO-);

Arylamincarbonyl: a mono- to trinuclear arylamino group (as mentioned above) which is linked to the skeleton via a carbonyl
5 group (-CO-);

Arylcarbonyloxy: a mono- to trinuclear aromatic ring system (as mentioned above) which is linked to the skeleton via a carbonyloxy group (-CO₂-);

10

Arylcarbonylthio: a mono- to trinuclear aromatic ring system (as mentioned above) which is linked to the skeleton via a carbonylthio group (-COS-);

15 Arylcarbonylamino: a mono- to trinuclear aromatic ring system (as mentioned above) which is linked to the skeleton via a carbonylamino group (-CONH-);

Arylsulfonyl: a mono- to trinuclear aromatic ring system (as
20 mentioned above) which is linked to the skeleton via a sulfonyl group (-SO₂-);

Aryloxysulfonyl: a mono- to trinuclear aryloxy group (as mentioned above) which is linked to the skeleton via a sulfonyl
25 group (-SO₂-);

Arylthiosulfonyl: a mono- to trinuclear arylthio group (as mentioned above) which is linked to the skeleton via a sulfonyl group (-SO₂-);

30

Arylaminosulfonyl: a mono- to trinuclear arylamino group (as mentioned above) which is linked to the skeleton via a sulfonyl group (-SO₂-);

35 Hetaryl:

- 5-membered hetaryl containing one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom: Hetaryl groups having 5 ring members which, in addition to carbon
40 nitrogen atoms and one sulfur or oxygen atom as ring members, for example 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl,
45 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl,

- 1,2,4-triazol-3-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl and 1,3,4-triazol-2-yl;
- benzo-fused 5-membered hetaryl containing one to three nitrogen atoms or one nitrogen atom and one oxygen or sulfur atom:
- 5 Hetaryl groups having 5 ring members which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members and in which two adjacent carbon ring members or one nitrogen and one adjacent carbon ring member may be bridged by
- 10 a buta-1,3-diene-1,4-diyl group;
- 5-membered hetaryl which is linked via nitrogen and contains one to four nitrogen atoms, or benzo-fused 5-membered hetaryl which is linked via nitrogen and contains one to three nitrogen atoms: Hetaryl groups having 5 ring members which, in addition
- 15 to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms as ring members and in which two adjacent carbon ring members or one nitrogen and one adjacent carbon ring member may be bridged by a buta-1,3-diene- 1,4-diyl group, these rings being linked to the skeleton via one of the
- 20 nitrogen ring members;
- 6-membered hetaryl containing one to three or one to four nitrogen atoms: Hetaryl groups having 6 ring members which, in addition to carbon atoms, may contain one to three or one to four nitrogen atoms as ring members, for example 2-pyridinyl,
- 25 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl and 1,2,4-triazin-3-yl;
- [insert (1) overleaf - not found]
- organic radical: alkyl, alkenyl, alkynyl, cycloalkyl,
- 30 heterocyclyl, aryl or hetaryl with or without substitution.

- With respect to alkyl, alkenyl and alkynyl groups, the term "unsubstituted or substituted" is meant to express that these groups may be partially or fully halogenated [i.e. the hydrogen
- 35 atoms of these groups may be partially or fully replaced by identical or different halogen atoms as mentioned above (preferably fluorine, chlorine or bromine)] and/or may carry one to three (preferably one) of the following radicals:
- cyano, nitro, hydroxyl, amino, formyl, carboxyl, aminocarbonyl,
- 40 alkoxy, haloalkoxy, alkylthio, haloalkylthio, alkylamino, dialkylamino, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy, alkylaminocarbonyl, dialkylaminocarbonyl, alkylcarbonylamino, alkoxycarbonylamino, alkylcarbonyl-N-alkylamino and
- 45 alkoxycarbonyl-N-alkylamino, where the alkyl groups in these radicals contain preferably 1 to 6, in particular 1 to 4, carbon atoms;

- cycloalkyl, cycloalkoxy, cycloalkylthio, cycloalkylamino, cycloalkyl-N-alkylamino, heterocyclyl, heterocyclyloxy, heterocyclylthio, heterocyclylamino or heterocyclyl-N-alkylamino unsubstituted or substituted by
- 5 customary groups, where the cyclic systems contain 3 to 12 ring members, preferably 2 to 8 ring members, in particular 3 to 6 ring members, and the alkyl groups in these radicals contain preferably 1 to 6 carbon atoms, in particular 1 to 4 carbon atoms;
- 10 - aryl, aryloxy, arylthio, arylamino, aryl-N-alkylamino, arylalkoxy, arylalkylthio, arylalkylamino, arylalkyl-N-alkylamino, hetaryl, hetaryloxy, hetarylthio, hetarylamino, hetaryl-N-alkylamino, hetarylalkoxy, hetarylalkylthio, hetarylalkylamino and
- 15 hetarylalkyl-N-alkylamino unsubstituted or substituted by customary groups, where the aryl radicals contain preferably 6 to 10 ring members, in particular 6 ring members (phenyl), the hetaryl radicals contain in particular 5 or 6 ring members and the alkyl groups in these radicals contain preferably 1 to 6
- 20 carbon atoms, in particular 1 to 4 carbon atoms.

- With respect to the *cyclic (saturated, unsaturated or aromatic) groups*, the term "*unsubstituted or substituted*" is meant to express that these groups may be partially or fully halogenated
- 25 [*i.e. the hydrogen atoms of these groups may be partially or fully replaced by identical or different halogen atoms as mentioned above (preferably fluorine, chlorine or bromine, in particular fluorine or chlorine)*] and/or may carry one to four (in particular one to three) of the following radicals:
- 30 - cyano, nitro, hydroxyl, amino, carboxyl, aminocarbonyl, alkyl, haloalkyl, alkenyl, haloalkenyl, alkenyloxy, haloalkenyloxy, alkynyl, haloalkynyl, alkynyloxy, haloalkynyloxy, alkoxy, haloalkoxy, alkylthio, halogenalkylthio, alkylamino, dialkylamino, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy,
 - 35 alkylaminocarbonyl, dialkylaminocarbonyl, alkylcarbonylamino, alkoxycarbonylamino, alkylcarbonyl-N-alkylamino and alkoxycarbonyl-N-alkylamino, where the alkyl groups in these radicals contain preferably 1 to 6 carbon atoms, in particular 1 to 4 carbon atoms and the alkenyl or alkynyl groups mentioned
 - 40 in these radicals contain 2 to 8, preferably 2 to 6, in particular 2 to 4, carbon atoms;
- and/or one to three (in particular one) of the following radicals:
- cycloalkyl, cycloalkoxy, cycloalkylthio, cycloalkylamino,
 - 45 cycloalkyl-N-alkylamino, heterocyclyl, heterocyclyloxy, heterocyclylthio, heterocyclylamino or heterocyclyl-N-alkylamino unsubstituted or substituted by

customary groups, where the cyclic systems contain 3 to 12 ring members, preferably 2 to 8 ring members, in particular 3 to 6 ring members, and the alkyl groups in these radicals contain preferably 1 to 6 carbon atoms, in particular 1 to 4 carbon atoms;

- 5 atoms;
 - aryl, aryloxy, arylthio, arylamino, aryl-N-alkylamino, arylalkoxy, arylalkylthio, arylalkylamino, arylalkyl-N-alkylamino, hetaryl, hetaryloxy, hetarylthio, hetarylamino, hetaryl-N-alkylamino, hetarylalkoxy, 10 hetarylalkylthio, hetarylalkylamino and hetarylalkyl-N-alkylamino unsubstituted or substituted by customary groups, where the aryl radicals contain preferably 6 to 10 ring members, in particular 6 ring members (phenyl), the hetaryl radicals contain in particular 5 or 6 ring members and 15 the alkyl groups in these radicals contain preferably 1 to 6 carbon atoms, in particular 1 to 4 carbon atoms and/or may carry one or two (in particular one) of the following radicals:
 - formyl,
 - 20 - CRⁱⁱⁱ=NOR^{iv} [where Rⁱⁱⁱ is hydrogen, alkyl, cycloalkyl and aryl and R^{iv} is alkyl, alkenyl, haloalkenyl, alkynyl and arylalkyl (where the abovementioned alkyl groups contain preferably 1 to 6 carbon atoms, in particular 1 to 4 carbon atoms, the abovementioned cycloalkyl groups, alkenyl groups and alkynyl 25 groups contain preferably 3 to 8, in particular 3 to 6, carbon atoms) and aryl is in particular phenyl which is unsubstituted or may be substituted by customary groups] or
 - NR^v-CO-D-R^{vi} [where R^v is hydrogen, hydroxyl, C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, C₁-C₆-alkoxy, C₂-C₆-alkenyloxy, 30 C₂-C₆-alkynyloxy, C₁-C₆-alkoxy-C₁-C₆-alkyl, C₁-C₆-alkoxy-C₁-C₆-alkoxy and C₁-C₆-alkoxycarbonyl, R^{vi} is hydrogen, C₁-C₆-alkyl, C₂-C₆-alkenyl, C₂-C₆-alkynyl, C₃-C₆-cycloalkyl, C₃-C₆-cycloalkenyl, aryl, aryl-C₁-C₆-alkyl, hetaryl and hetaryl-C₁-C₆-alkyl and D is a direct bond, oxygen 35 or nitrogen, where the nitrogen may carry one of the groups mentioned under R^{vi}],
- and/or where two adjacent carbon atoms of the cyclic systems may carry a C₃-C₅-alkylene, C₃-C₅-alkenylene, oxy-C₂-C₄-alkylene, oxy-C₁-C₃-alkyleneoxy, oxy-C₂-C₄-alkenylene, 40 oxy-C₂-C₄-alkenyleneoxy or butadienediyl group, where these bridges may for their part be partially or fully halogenated and/or may carry one to three, in particular one or two, of the following radicals:
- C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy and 45 C₁-C₄-alkylthio.

14

Customary groups are in particular the following substituents: halogen, cyano, nitro, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₁-C₄-alkylamino, di-C₁-C₄-alkylamino and C₁-C₄-alkylthio.

5

Unsubstituted or substituted phenyl is to be understood as meaning, in particular, a halogen-, cyano-, nitro-, hydroxy-, amino-, carboxyl-, aminocarbonyl-, C₁-C₄-alkyl- or halo-C₁-C₄-alkyl-substituted phenyl ring.

10

With respect to the intended use of the 5-hydroxypyrazolines of the formula I, particular preference is given to the following meanings of the substituents, in each case both on their own or in combination:

15

Particular preference is given to compounds IA.

Moreover, particular preference is given to compounds of the formula IB in which A' is SO₂.

20

Likewise, particular preference is given to compounds of the formula IB in which A' is C = S.

Additionally, particular preference is given to compounds I in which R¹ is C₁-C₄-haloalkyl.

Particular preference is also given to compounds I in which R¹ is C₃F₇ or C₂F₅.

Moreover, particular preference is given to compounds I in which R¹ is unsubstituted or substituted phenyl.

Likewise, particular preference is given to compounds I in which B is phenyl which carries a substituent in the 2-position.

35

Moreover, particular preference is given to compounds I in which B is phenyl which carries a substituent in the 4-position.

Furthermore, particular preference is given to compounds I in which B is phenyl which carries substituents in the 3,4-position.

Additionally, particular preference is given to compounds I in which B is hetaryl.

Furthermore, particular preference is given to compounds I in which R² and R³ are each hydrogen.

15

Moreover, particular preference is given to compounds I in which R^4 is hydrogen or methyl.

Likewise, particular preference is given to compounds I in which R^4 is trifluoromethyl.

Additionally, particular preference is given to compounds I in which the substituents R^1 and R^4 are different.

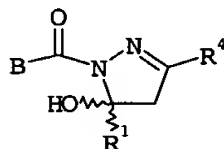
10 With respect to their use, particular preference is given to the compounds I compiled in the tables below. Moreover, the groups mentioned for a substituent in the tables are, by themselves and independently of the combination in which they are mentioned, a particularly preferred embodiment of the substituent in question.

15

Table 1

Compounds of the formula IA', in which R^1 is C_2F_5 , R^4 is methyl and B corresponds for each compound to a row of Table A

20



IA'

25 Table 2

Compounds of the formula IA', in which R^1 is C_2F_5 , R^4 is ethyl and B corresponds for each compound to a row of Table A

Table 3

30 Compounds of the formula IA', in which R^1 is C_3F_7 , R^4 is methyl and B corresponds for each compound to a row of Table A

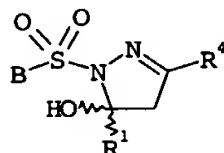
Table 4

Compounds of the formula IA', in which R^1 is C_3F_7 , R^4 is ethyl and B corresponds for each compound to a row of Table A

40 Table 5

Compounds of the formula IB.1', in which R^1 is C_2F_5 , R^4 is methyl and B corresponds for each compound to a row of Table A

45



IB.1'

45 Table 6

Compounds of the formula IB.1', in which R^1 is C_2F_5 , R^4 is ethyl

and B corresponds for each compound to a row of Table A

Table 7

Compounds of the formula IB.1', in which R¹ is C₃F₇, R⁴ is methyl
5 and B corresponds for each compound to a row of Table A

Table 8

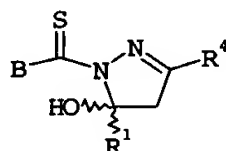
Compounds of the formula IB.1', in which R¹ is C₃F₇, R⁴ is ethyl
and B corresponds for each compound to a row of Table A

10

Table 9

Compounds of the formula IB.2', in which R¹ is C₂F₅, R⁴ is methyl
and B corresponds for each compound to a row of Table A

15



IB.2'

Table 10

20 Compounds of the formula IB.2', in which R¹ is C₂F₅, R⁴ is ethyl
and B corresponds for each compound to a row of Table A

Table 11

Compounds of the formula IB.2', in which R¹ is C₃F₇, R⁴ is methyl
25 and B corresponds for each compound to a row of Table A

Table 12

Compounds of the formula IB.2', in which R¹ is C₃F₇, R⁴ is ethyl
and B corresponds for each compound to a row of Table A

30

Table A

No.	B
A-1	C ₆ H ₅
35 A-2	2-F-C ₆ H ₄
A-3	3-F-C ₆ H ₄
A-4	4-F-C ₆ H ₄
A-5	2-Cl-C ₆ H ₄
40 A-6	3-Cl-C ₆ H ₄
A-7	4-Cl-C ₆ H ₄
A-8	2-Br-C ₆ H ₄
A-9	3-Br-C ₆ H ₄
A-10	4-Br-C ₆ H ₄
45 A-11	2-OH-C ₆ H ₄
A-12	3-OH-C ₆ H ₄

	No.	B
	A-13	4-OH-C ₆ H ₄
	A-14	2-NO ₂ -C ₆ H ₄
5	A-15	3-NO ₂ -C ₆ H ₄
	A-16	4-NO ₂ -C ₆ H ₄
	A-17	2-CN-C ₆ H ₄
	A-18	3-CN-C ₆ H ₄
10	A-19	4-CN-C ₆ H ₄
	A-20	2-NH ₂ -C ₆ H ₄
	A-21	3-NH ₂ -C ₆ H ₄
	A-22	4-NH ₂ -C ₆ H ₄
	A-23	2-N(CH ₃) ₂ -C ₆ H ₄
15	A-24	3-N(CH ₃) ₂ -C ₆ H ₄
	A-25	4-N(CH ₃) ₂ -C ₆ H ₄
	A-26	2-N(CH ₂ CH ₃) ₂ -C ₆ H ₄
	A-27	3-N(CH ₂ CH ₃) ₂ -C ₆ H ₄
20	A-28	4-N(CH ₂ CH ₃) ₂ -C ₆ H ₄
	A-29	2-CH ₃ -C ₆ H ₄
	A-30	3-CH ₃ -C ₆ H ₄
	A-31	4-CH ₃ -C ₆ H ₄
25	A-32	2-CH ₂ CH ₃ -C ₆ H ₄
	A-33	3-CH ₂ CH ₃ -C ₆ H ₄
	A-34	4-CH ₂ CH ₃ -C ₆ H ₄
	A-35	2-OCH ₃ -C ₆ H ₄
	A-36	3-OCH ₃ -C ₆ H ₄
30	A-37	4-OCH ₃ -C ₆ H ₄
	A-38	2-OCH ₂ CH ₃ -C ₆ H ₄
	A-39	3-OCH ₂ CH ₃ -C ₆ H ₄
	A-40	4-OCH ₂ CH ₃ -C ₆ H ₄
35	A-41	2-(O-C ₆ H ₅)-C ₆ H ₄
	A-42	3-(O-C ₆ H ₅)-C ₆ H ₄
	A-43	4-(O-C ₆ H ₅)-C ₆ H ₄
	A-44	2,4-F ₂ -C ₆ H ₃
40	A-45	3,5-F ₂ -C ₆ H ₃
	A-46	2,4-Cl ₂ -C ₆ H ₃
	A-47	3,5-Cl ₂ -C ₆ H ₃
	A-48	2,4-Br ₂ -C ₆ H ₃
45	A-49	3,5-Br ₂ -C ₆ H ₃
	A-50	2-F-4-Cl-C ₆ H ₃
	A-51	3-F-5-Cl-C ₆ H ₃

No.	B
A-52	2-F-4-Br-C ₆ H ₃
A-53	3-F-5-Br-C ₆ H ₃
5	A-54 2-Cl-4-F-C ₆ H ₃
A-55	3-Cl-5-F-C ₆ H ₃
A-56	2-Cl-4-Br-C ₆ H ₃
A-57	3-Cl-5-Br-C ₆ H ₃
10	A-58 2-Br-4-F-C ₆ H ₃
A-59	3-Br-5-F-C ₆ H ₃
A-60	2-Br-4-Cl-C ₆ H ₃
A-61	3-Br-5-Cl-C ₆ H ₃

- 15 The compounds I are suitable for use as fungicides. They have excellent activity against a broad spectrum of phytopathogenic fungi, in particular from the classes of the *Ascomycetes*, *Deuteromycetes*, *Phycomycetes* and *Basidiomycetes*. Some of them act systemically and can be employed in crop protection as foliar-
20 and soil-acting fungicides.

They are especially important for controlling a large number of fungi in a variety of crop plants such as wheat, rye, barley, oats, rice, maize, grass, bananas, cotton, soya, coffee, sugar
25 cane, grape vines, fruit species, ornamentals and vegetable species such as cucumbers, beans, tomatoes, potatoes and cucurbits, and also in the seeds of these plants.

- Specifically, they are suitable for controlling the following
30 plant diseases:
- Alternaria species in vegetables and fruit,
 - Botrytis cinerea (gray mold) in strawberries, vegetables, orna-
mentals and grape vines,
 - Cercospora arachidicola in groundnuts,
 - 35 Erysiphe cichoracearum and Sphaerotheca fuliginea in cucurbits,
 - Erysiphe graminis (powdery mildew) in cereals,
 - Fusarium and Verticillium species in a variety of plants,
 - Helminthosporium species in cereals,
 - Mycosphaerella species in bananas and ground nuts,
 - 40 Phytophthora infestans in potatoes and tomatoes,
 - Plasmopara viticola in grape vines,
 - Podosphaera leucotricha in apples,
 - Pseudocercospora herpotrichoides in wheat and barley,
 - Pseudoperonospora species in hops and cucumbers,
 - 45 Puccinia species in cereals,
 - Pyricularia oryzae in rice,
 - Rhizoctonia species in cotton, rice and lawns,

Septoria nodorum in wheat,
Uncinula necator in grape vines,
Ustilago species in cereals and sugar cane, and
Venturia species (scab) in apples and pears.

5

The compounds I are employed by treating the fungi or the plants, seeds, materials or the soil to be protected against fungal attack with a fungicidally effective amount of the active compounds. The application can be carried out before or after the
10 infection of the materials, plants or seeds by the fungi.

The fungicidal compositions generally comprise from 0.1 to 95, preferably from 0.5 to 90, % by weight of active compound.

15 For use in crop protection, the application rates are, depending on the kind of effect desired, from 0.01 to 2.0 kg of active compound per ha.

The treatment of seeds generally requires active compound
20 quantities of from 0.001 to 0.1 g, preferably from 0.01 to 0.05 g, per kilogram of seed.

For use in the protection of materials or stored products, the active compound application rate depends on the kind of
25 application area and effect desired. Customary application rates in the protection of materials are, for example, from 0.001 g to 2 kg, preferably from 0.005 g to 1 kg, of active compound per cubic meter of treated material.

30 The compounds I can be converted into the customary formulations, eg. solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the specific intended use; in any case, it should guarantee fine and uniform distribution of the compound according to the invention.

35

The formulations are prepared in a known manner, eg. by extending the active compound with solvents and/or carriers, if desired using emulsifiers and dispersants, it being possible to use other organic solvents as auxiliary solvents if water is used as the
40 diluent. Suitable auxiliaries for this purpose are essentially: solvents such as aromatics (eg. xylene), chlorinated aromatics (eg. chlorobenzenes), paraffins (eg. mineral oil fractions), alcohols (eg. methanol, butanol), ketones (eg. cyclohexanone), amines (eg. ethanolamine, dimethylformamide) and water; carriers
45 such as ground natural minerals (eg. kaolin, clays, talc, chalk) and ground synthetic minerals (eg. finely divided silica, silicates); emulsifiers such as nonionic and anionic emulsifiers

(eg. polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates), and dispersants such as lignin-sulfite waste liquors and methylcellulose.

- 5 Suitable surfactants are the alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, and dibutyl naphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates and fatty acids and alkali metal salts and
- 10 alkaline earth metal salts thereof, salts of sulfated fatty alcohol glycol ethers, condensation products of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensation products of naphthalene or of naphthalene sulfonic acid with phenol and formaldehyde, polyoxyethylene octylphenol
- 15 ethers, ethoxylated isooctylphenol, octylphenol and nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene,
- 20 lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and methylcellulose.

- Suitable for preparing directly sprayable solutions, emulsions, pastes or oil dispersions are petroleum fractions having medium
- 25 to high boiling points, such as kerosine or diesel fuel, furthermore coal-tar oils and oils of plant or animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example benzene, toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or derivatives thereof, methanol, ethanol, propanol,
- 30 butanol, chloroform, carbon tetrachloride, cyclohexanol, cyclohexanone, chlorobenzene, isophorone, strongly polar solvents, for example dimethylformamide, dimethyl sulfoxide, N-methylpyrrolidone, and water.

- 35 Powders, compositions for broadcasting and dusts can be prepared by mixing or joint grinding the active substances with a solid carrier.

- Granules, for example coated granules, impregnated granules and
- 40 homogeneous granules, can be prepared by binding the active compounds to solid carriers. Solid carriers are, for example, mineral earths, such as silica gel, silicas, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate,
- 45 magnesium oxide, ground synthetic materials, fertilizers, such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas and products of vegetable origin, such as cereal meal, tree bark

meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

The formulations generally comprise from 0.01 to 95 % by weight, preferably from 0.1 to 90 % by weight, of the active compound. The active compounds are employed in a purity of from 90 % to 100 %, preferably from 95 % to 100 % (according to the NMR spectrum).

10 Examples of formulations are:

- I. 5 parts by weight of a compound according to the invention are thoroughly mixed with 95 parts by weight of finely divided kaolin. This affords a dusting composition comprising 5 % by weight of the active compound.
- II. 30 parts by weight of a compound according to the invention are thoroughly mixed with a mixture of 92 parts by weight of pulverulent silica gel and 8 parts by weight of paraffin oil which had been sprayed onto the surface of this silica gel. This affords an active compound preparation having good adhesive properties (active compound content 23 % by weight).
- III. 10 parts by weight of a compound according to the invention are dissolved in a mixture comprising 90 parts by weight of xylene, 6 parts by weight of the addition product of 8 to 10 mol of ethylene oxide to 1 mol of oleic acid N-monoethanolamide, 2 parts by weight of the calcium salt of dodecylbenzenesulfonic acid and 2 parts by weight of the addition product of 40 mol of ethylene oxide to 1 mol of castor oil (active compound content 9 % by weight).
- IV. 20 parts by weight of a compound according to the invention are dissolved in a mixture comprising 60 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 5 parts by weight of the addition product of 7 mol of ethylene oxide to 1 mol of isooctylphenol and 5 parts by weight of the addition product of 40 mol of ethylene oxide to 1 mol of castor oil (active compound content 16 % by weight).
- V. 80 parts by weight of a compound according to the invention are mixed well with 3 parts by weight of the sodium salt of diisobutyl-naphthalene- α -sulfonic acid, 10 parts by weight of the sodium salt of a lignosulfonic

acid from a sulfite waste liquor and 7 parts by weight of pulverulent silica gel, and ground in a hammer mill (active compound content 80 % by weight).

- 5 VI. 90 parts by weight of a compound according to the invention are mixed with 10 parts by weight of N-methyl- α -pyrrolidone, affording a solution which is suitable for use in the form of very small drops (active compound content 90 % by weight).
- 10 VII. 20 parts by weight of a compound according to the invention are dissolved in a mixture comprising 40 parts by weight of cyclohexanone, 30 parts by weight of isobutanol, 20 parts by weight of the addition product of 15 7 mol of ethylene oxide to 1 mol of isooctylphenol and 10 parts by weight of the addition product of 40 mol of ethylene oxide to 1 mol of castor oil. The solution is poured into 100,000 parts by weight of water and finely dispersed therein, affording an aqueous dispersion 20 comprising 0.02 % by weight of active compound.
- VIII. 20 parts by weight of a compound according to the invention are mixed well with 3 parts by weight of the sodium salt of diisobutyl-naphthalene- α -sulfonic acid, 25 17 parts by weight of the sodium salt of a lignosulfonic acid from a sulfite waste liquor and 60 parts by weight of pulverulent silica gel, and ground in a hammer mill. The mixture is finely dispersed in 20,000 parts by weight of water, affording a spray liquor comprising 0.1 % by 30 weight of active compound.

The active compounds can be applied as such, in the form of their formulations or in the application forms prepared therefrom, for example in the form of directly sprayable solutions, powders, 35 suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, compositions for broadcasting, or granules, by spraying, atomizing, dusting, broadcasting or watering. The application forms depend entirely on the intended uses; in any case, they should ensure very fine dispersion of the active compounds 40 according to the invention.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (spray powders, oil dispersions) by addition of water. To prepare emulsions, pastes or oil 45 dispersions, the substances can be homogenized in water as such or dissolved in an oil or solvent, by means of wetting agents, tackifiers, dispersants or emulsifiers. However, concentrates

comprising active compound, wetting agent, tackifier, dispersant or emulsifier and possibly solvent or oil which are suitable for dilution with water can also be prepared.

- 5 The active compound concentrations in the ready-to-use preparations can be varied over a relatively wide range. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

It is also possible to use the active compounds with good success
10 in the ultra-low-volume method (ULV), it being possible to apply formulations comprising more than 95 % by weight of active compound or even the active compound without additives.

Oils of various types, herbicides, fungicides, other pesticides
15 and bactericides can be added to the active compounds, if desired even immediately prior to application (tank mix). These agents can be added to the compositions according to the invention in a weight ratio of 1:10 to 10:1.

- 20 The compositions according to the invention in the use form as fungicides may also be present in combination with other active compounds, for example with herbicides, insecticides, growth regulators, fungicides or else with fertilizers. In many cases, a mixture of the compounds I, or of the compositions comprising
25 them, in the use form as fungicides with other fungicides results in a broader fungicidal spectrum of activity.

The following list of fungicides in combination with which the compounds according to the invention can be used is intended to
30 illustrate the possible combinations, but not to impose any limitation:

- sulfur, dithiocarbamates and their derivatives, such as iron(III) dimethyldithiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisdithiocarbamate,
35 manganese ethylenebisdithiocarbamate, manganese zinc ethylenediaminebisdithiocarbamate, tetramethylthiuram disulfide, ammonia complex of zinc (N,N-ethylenebisdithiocarbamate), ammonia complex of zinc (N,N'-propylenebisdithiocarbamate), zinc
40 (N,N'-propylenebisdithiocarbamate), N,N'-polypropylenebis(thiocarbamoyl)disulfide;
- nitro derivatives, such as dinitro-(1-methylheptyl)phenyl crotonate, 2-sec-butyl-4,6-dinitrophenyl-3,3-dimethyl acrylate, 2-sec-butyl-4,6-dinitrophenylisopropyl carbonate, diisopropyl
45 5-nitroisophthalate;

- heterocyclic substances, such as 2-heptadecyl-2-imidazoline acetate, 2,4-dichloro-6-(o-chloroanilino)-s-triazine, O,O-diethyl phthalimidophosphonothioate, 5-amino-1-[bis(dimethylamino)phosphinyl]-3-phenyl-1,2,4-
- 5 triazole, 2,3-dicyano-1,4-dithioanthraquinone, 2-thio-1,3-dithiolo[4,5-b]quinoxaline, methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, 2-methoxycarbonylamino benzimidazole, 2-(furyl-(2))benzimidazole, 2-(thiazolyl-(4))benzimidazole,
- 10 N-(1,1,2,2-tetrachloroethylthio)tetrahydrophthalimide, N-trichloromethylthiotetrahydrophthalimide, N-trichloromethylthiophthalimide,
- N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfuric diamide, 5-ethoxy-3-trichloromethyl-1,2,3-thiadiazole,
- 15 2-thiocyanatomethylthiobenzothiazole, 1,4-dichloro-2,5-dimethoxybenzene, 4-(2-chlorophenylhydrazono)-3-methyl-5-isoxazolone, pyridine 2-thio-1-oxide, 8-hydroxyquinoline or its copper salt, 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine,
- 20 2,3-dihydro-5-carboxanilido-6-methyl-1,4-oxathiine-4,4-dioxide, 2-methyl-5,6-dihydro-4H-pyran-3-carboxanilide, 2-methylfuran-3-carboxanilide, 2,5-dimethylfuran-3-carboxanilide, 2,4,5-trimethylfuran-3-carboxanilide,
- 25 N-cyclohexyl-2,5-dimethylfuran-3-carboxamide, N-cyclohexyl-N-methoxy-2,5-dimethylfuran-3-carboxamide, 2-methylbenzanilide, 2-iodobenzanilide, N-formyl-N-morpholine 2,2,2-trichloroethyl acetal, piperazine-1,4-diyl-bis-1-(2,2,2-trichloroethyl)formamide, 1-(3,4-dichloroanilino)-1-
- 30 formylamino-2,2,2-trichloroethane, 2,6-dimethyl-N-tridecylmorpholine or its salts, 2,6-dimethyl-N-cyclododecylmorpholine or its salts, N-[3-(p-tert-butylphenyl)-2-methylpropyl]-cis-2,6-dimethylmorpholine, N-[3-(p-tert-butylphenyl)-2-methyl-
- 35 propyl]piperidine, 1-[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl-ethyl]-1H-1,2,4-triazole, 1-[2-(2,4-dichlorophenyl)-4-n-propyl-1,3-dioxolan-2-ylethyl]-1H-1,2,4-triazole, N-(n-propyl)-N-(2,4,6-trichlorophenoxyethyl)-N'-imidazolylurea, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-
- 40 yl)-2-butanone, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl)-2-butanol, (2RS, 3RS)-1-[3-(2-chlorophenyl)-2-(4-fluorophenyl)oxiran-2-ylmethyl]-1H-1,2,4-triazole, α -(2-chlorophenyl)- α -(4-chlorophenyl)-5-pyrimidine-methanol, 5-butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine,
- 45 bis(p-chlorophenyl)-3-pyridinemethanol, 1,2-bis(3-ethoxycarbonyl-2-thioureido)benzene, 1,2-bis-(3-methoxycarbonyl-2-thioureido)benzene,

25

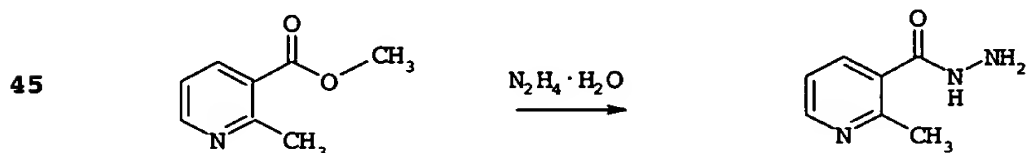
- strobilurins, such as methyl E-methoximino-[α -(o-tolyloxy)-o-tolyl]acetate, methyl E-2-[2-[6-(2-cyanophenoxy)-pyridimin-4-yloxy]-phenyl]-3-methoxyacrylate, methyl E-methoximino-[α -(2-phenoxyphenyl)]acetamide,
- 5 methyl-E-methoximino-[α -(2,5-dimethylphenoxy)-o-tolyl]acetamide,
- anilinopyrimidines, such as N-(4,6-dimethylpyrimidin-2-yl)aniline, N-[4-methyl-6-(1-propynyl)pyrimidin-2-yl]aniline, N-(4-methyl-6-cyclopropylpyrimidin-2-yl)aniline,
- 10 • phenylpyrroles, such as 4-(2,2-difluoro-1,3-benzodioxol-4-yl)pyrrole-3-carbonitrile,
- cinnamamides, such as 3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)acryloylmorpholine,
- and a variety of fungicides, such as dodecylguanidine acetate,
- 15 3-[3-(3,5-dimethyl-2-oxycyclohexyl)-2-hydroxyethyl]glutarimide, hexachlorobenzene, methyl N-(2,6-dimethylphenyl)-N-(2-furoyl)-DL-alaninate, DL-N-(2,6-dimethylphenyl)-N-(2'-methoxyacetyl)-alanine methyl ester, N-(2,6-dimethylphenyl)-N-chloroacetyl-D,L-2-aminobutyrolactone,
- 20 DL-N-(2,6-dimethylphenyl)-N-(phenylacetyl)alanine methyl ester, 5-methyl-5-vinyl-3-(3,5-dichlorophenyl)-2,4-dioxo-1,3-oxazolidine, 3-(3,5-dichlorophenyl)-5-methyl-5-methoxymethyl-1,3-oxazolidine-2,4-dione, 3-(3,5-dichlorophenyl)-1-isopropylcarbamoylethylhydantoin,
- 25 N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide, 2-cyano-[N-(ethylaminocarbonyl)-2-methoximino]-acetamide, 1-[2-(2,4-dichlorophenyl)pentyl]-1H-1,2,4-triazole, 2,4-difluoro- α -(1H-1,2,4-triazolyl-1-methyl)benzhydryl alcohol, N-(3-chloro-2,6-dinitro-4-trifluoromethylphenyl)-5-trifluoro-
- 30 methyl-3-chloro-2-aminopyridine, 1-((bis-(4-fluorophenyl)-methylsilyl)methyl)-1H-1,2,4-triazole.

Synthesis examples

- 35 The procedures given in the synthesis examples below were used to obtain further compounds I by appropriate modification of the starting materials. The compounds obtained in this manner are listed in the tables that follow, together with physical data.

40 A) Preparation of the precursors

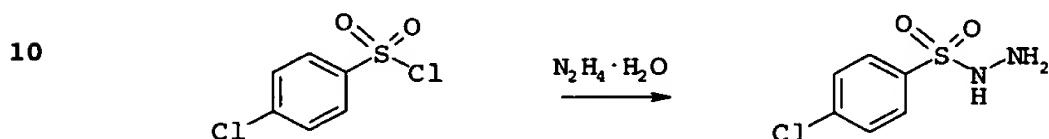
Example 1 Preparation of 2-methylpyridine-3-carbohydrazide



26

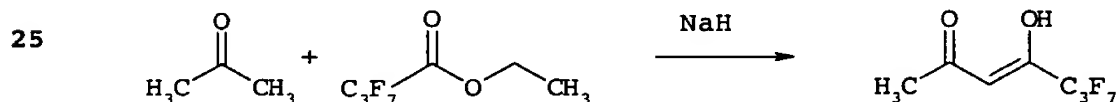
A solution of 1 g of methyl 2-methylpyridine-3-carboxyate in 5 ml of methanol was admixed with 3 g of hydrazine hydrate and then stirred at 20 - 25°C for 14 hours. The mixture was diluted with water and extracted with methylene chloride. The solvent was distilled off from the combined organic phases, giving 0.45 g of title compound as colorless crystals of m.p. 60°C.

Example 2 Preparation of 4-chlorophenylsulfohydrazide



At 10 to 20°C, 24 g (0.48 mol) of hydrazine hydrate, dissolved in 25 ml of water, were added dropwise to a solution of 50 g (0.24 mol) of 4-chlorophenylsulfonyl chloride in 300 ml of THF. The reaction mixture was stirred at approximately 15°C for 15 min and then poured onto ice. The solution was concentrated and the precipitate was filtered off. 40 g of the title compound were isolated as colorless crystals of m.p. 79°C.

Example 3 Preparation of 5,5,6,6,7,7,7-heptafluoro-2,4-heptanedione



At 30°C, 4.1 g (170 mmol) of sodium hydride (97%) in 45 ml of anhydrous cyclohexane were admixed with a solution of 68.4 g (300 mmol) of methyl perfluorobutyrate and 8.7 g (150 mmol) of anhydrous acetone. The mixture was stirred at 20 - 25°C for 14 hours and then diluted with distilled water and acidified with dilute hydrochloric acid. The phases were separated and the aqueous phase was extracted with diethyl ether. The combined organic phases were washed with water and then fractionated over a 40 cm Vigreux column. This gave 22 g of the title compound as a colorless liquid of b.p. 135°C.

¹H NMR (CDCl₃): δ (ppm) = 2.1 (s, 3H); 5.95 (s, 1H).

40

Example 4 Preparation of 5,5,6,6,6-pentafluoro-2,4-hexanedione

Using the conditions mentioned in Example 3, 2.7 g of sodium hydride and 27 ml of cyclohexane were reacted with 5.8 g (100 mmol) of acetone and 38.4 g (200 mmol) of ethyl

27

perfluoropropionate, giving 19.4 g of the title compound as a colorless liquid of b.p. 119°C.

^1H NMR (CDCl_3): δ (ppm) = 2.1 (s, 3H); 5.95 (s, 1H).

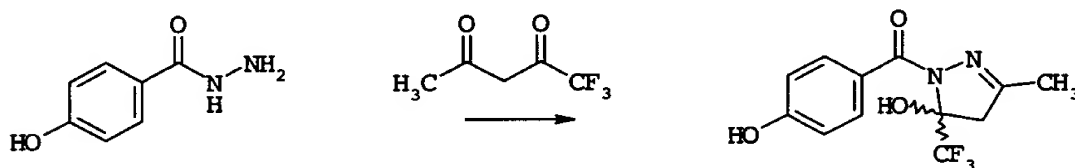
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B) Preparation of the active compounds

Example 4 Preparation of
5-hydroxy-5-trifluoromethyl-3-methyl-4,5-dihydro-
pyrazol-1-yl-(4-hydroxyphenyl)methanone [I-73]

10

15



20

A solution of 5 g (33 mmol) of 4-hydroxybenzhydrazide and 5 g (33 mmol) of trifluoroacetylacetone in 100 ml of ethanol was heated at 70°C for 6 hours. The solvent was distilled off, giving 9.0 g of the title compound as colorless crystals.

Example 5 Preparation of
5-hydroxy-5-(1,1,1,2,2-pentafluoroethyl)-3-methyl-
4,5-dihydropyrazol-1-yl-(4-bromophenyl)methanone [I-13]

25

Using the conditions mentioned in Example 4, reaction of 1 g (5 mmol) of 4-bromobenzhydrazide with 1 g (5 mmol) of 5,5,6,6,6-pentafluoro-2,4-hexanedione in 100 ml of ethanol gave 1.9 g of the title compound as colorless crystals.

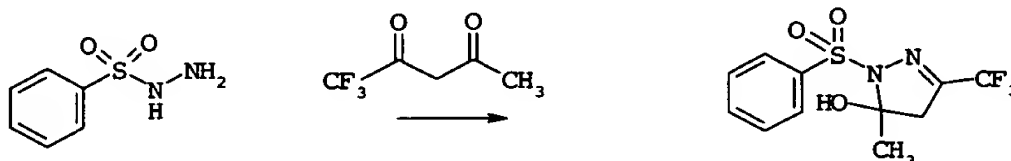
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Example 6 Preparation of
5-hydroxy-5-(1,1,1,2,2,3,3-heptafluoropropyl)-3-methyl-
4,5-dihydropyrazol-1-yl-phenylmethanone [I-35]

35 Using the conditions mentioned in Example 4, reaction of 0.8 g (6 mmol) of benzhydrazide with 1.5 g (6 mmol) of 5,5,6,6,7,7,7-heptafluoro-2,4-heptanedione in 100 ml of ethanol gave 9.0 g of the title compound as colorless crystals.

40 Example 7 Preparation of
2-benzenesulfonyl-3-trifluoromethyl-5-methyl-3,4-
dihydro-2H-pyrazol-3-ol [II-1]

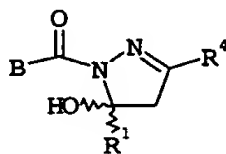
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28

A solution of 1 g (6 mmol) of benzenesulfohydrazide and 0.9 g (6 mmol) of trifluoroacetylacetone in ethanol was heated at 70°C for 6 hours. The solvent was distilled off, giving 1.6 g of the title compound as colorless crystals.

5 Table I



IA'

10

No.	B	R ¹	R ⁴	Phys. data (m.p. [°C])
I-1	phenyl	3-NO ₂ -phenyl	COOCH ₃	136-139
I-2	phenyl	3-NO ₂ -phenyl	CH ₃	133-137
I-3	phenyl	4-Br-phenyl	CH ₃	176-180
I-4	phenyl	4-Cl-phenyl	CH ₃	172-178
I-5	2-OH-phenyl	4-F-phenyl	CH ₃	oil
I-6	phenyl	4-NO ₂ -phenyl	COOCH ₃	179-183
I-7	4-NO ₂ -phenyl	4-NO ₂ -phenyl	CH ₃	>200
I-8	2-OH-phenyl	C ₂ F ₅	CF ₃	96
I-9	2-OH-phenyl	C ₂ F ₅	CH ₃	173
I-10	3-Cl-phenyl	C ₂ F ₅	CH ₃	120
I-11	3-CH ₃ -phenyl	C ₂ F ₅	CH ₃	144
I-12	3-OH-phenyl	C ₂ F ₅	CH ₃	83
I-13	4-Br-phenyl	C ₂ F ₅	CH ₃	135
I-14	4-Cl-phenyl	C ₂ F ₅	CH ₃	110
I-15	4-CN-phenyl	C ₂ F ₅	CH ₃	98
I-16	4-F-phenyl	C ₂ F ₅	CH ₃	123
I-17	4-OH-phenyl	C ₂ F ₅	CH ₃	141
I-18	2-OH-phenyl	C ₂ F ₅	tert-butyl	oil
I-19	3-CH ₃ -phenyl	C ₂ F ₅	tert-butyl	72
I-20	4-Br-phenyl	C ₂ F ₅	tert-butyl	150
I-21	2-OH-phenyl	C ₃ F ₇	2-thienyl	oil
I-22	2-OH-phenyl	C ₃ F ₇	CF ₃	120
I-23	3-CH ₃ -phenyl	C ₃ F ₇	CF ₃	73
I-24	4-Br-phenyl	C ₃ F ₇	CF ₃	128
I-25	2-OH-phenyl	C ₃ F ₇	CH ₃	145
I-26	3-Br-phenyl	C ₃ F ₇	CH ₃	88
I-27	3-Cl-phenyl	C ₃ F ₇	CH ₃	99
I-28	3-CH ₃ -phenyl	C ₃ F ₇	CH ₃	95
I-29	3-NO ₂ -phenyl	C ₃ F ₇	CH ₃	100

	No.	B	R ¹	R ⁴	Phys. data (m.p. [°C])
5	I-30	4-Br-phenyl	C ₃ F ₇	CH ₃	117
	I-31	4-Cl-phenyl	C ₃ F ₇	CH ₃	120
	I-32	4-CN-phenyl	C ₃ F ₇	CH ₃	115
	I-33	4-F-phenyl	C ₃ F ₇	CH ₃	145
	I-34	4-OCH ₃ -phenyl	C ₃ F ₇	CH ₃	121
10	I-35	phenyl	C ₃ F ₇	CH ₃	129
	I-36	3-CH ₃ -phenyl	C ₃ F ₇	2-thienyl	75
	I-37	2-OH-phenyl	CF ₃	2-thienyl	oil
	I-38	4-Br-phenyl	CF ₃	2-thienyl	128
	I-39	2-OH, 5-Cl-phenyl	CF ₃	CF ₃	70
15	I-40	3-pyridyl	CF ₃	CF ₃	128
	I-41	4-Br-phenyl	CF ₃	CF ₃	139
	I-42	4-pyridyl	CF ₃	CF ₃	160
	I-43	6-CH ₃ -pyridyl-2	CF ₃	CF ₃	95
	I-44	2-OH-phenyl	CF ₃	iPr	oil
20	I-45	4-Br-phenyl	CF ₃	iPr	94
	I-46	1-naphthyl	CF ₃	CH ₃	156
	I-47	2,4-Cl ₂ -phenyl	CF ₃	CH ₃	153
	I-48	2,5-Cl ₂ -phenyl	CF ₃	CH ₃	124
	I-49	2-Cl-phenyl	CF ₃	CH ₃	100
25	I-50	2-F, 6-NH ₂ -phenyl	CF ₃	CH ₃	97
	I-51	2-CH ₃ -pyridyl-3	CF ₃	CH ₃	116
	I-52	2-OH, 5-Cl-phenyl	CF ₃	CH ₃	140
	I-53	2-OH-naphthyl	CF ₃	CH ₃	209
	I-54	2-OH-phenyl	CF ₃	CH ₃	150
30	I-55	3,5-(CF ₃) ₂ -phenyl	CF ₃	CH ₃	100
	I-56	3,4,5-(OCH ₃) ₃ -phenyl	CF ₃	CH ₃	121
	I-57	3,4-Cl ₂ -phenyl	CF ₃	CH ₃	107
	I-58	3,5-(OH) ₂ -phenyl	CF ₃	CH ₃	75
	I-59	3-Br-phenyl	CF ₃	CH ₃	61-67
40	I-60	3-Cl-phenyl	CF ₃	CH ₃	oil
	I-61	3-CH ₃ -phenyl	CF ₃	CH ₃	58
	I-62	3-NH ₂ , 4-OH-phenyl	CF ₃	CH ₃	123
	I-63	3-NO ₂ -phenyl	CF ₃	CH ₃	82
	I-64	3-OH-phenyl	CF ₃	CH ₃	oil
45	I-65	3-pyridyl	CF ₃	CH ₃	68
	I-66	4-Br-phenyl	CF ₃	CH ₃	116
	I-67	4-CF ₃ -phenyl	CF ₃	CH ₃	56

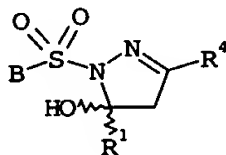
	No.	B	R ¹	R ⁴	Phys. data (m.p. [°C])
5	I-68	4-Cl-phenyl	CF ₃	CH ₃	95
	I-69	4-CN-phenyl	CF ₃	CH ₃	134
	I-70	4-F-phenyl	CF ₃	CH ₃	63
	I-71	4-CH ₃ -phenyl	CF ₃	CH ₃	89
	I-72	4-NO ₂ -phenyl	CF ₃	CH ₃	110
10	I-73	4-OH-phenyl	CF ₃	CH ₃	120
	I-74	4-OCH ₃ -phenyl	CF ₃	CH ₃	oil
	I-75	4-phenylphenyl	CF ₃	CH ₃	146
	I-76	4-pyridyl	CF ₃	CH ₃	103
15	I-77	4-tert-butyl-phenyl	CF ₃	CH ₃	96
	I-78	6-Cl-pyridyl -2	CF ₃	CH ₃	oil
	I-79	6-CH ₃ -pyridyl-2	CH ₃	CF ₃	90
	I-80	phenyl	CF ₃	CH ₃	65
20	I-81	2-OH-phenyl	CF ₃	tert-butyl	123
	I-82	3-CH ₃ -phenyl	CF ₃	tert-butyl	86
	I-83	2-NH ₂ -phenyl	CH ₃	CH ₃	122-128
	I-84	2-OH, 4-Cl-phenyl	CH ₃	CH ₃	130
	I-85	2-OH-phenyl	CH ₃	CH ₃	oil
25	I-86	3,4,5-(OCH ₃) ₃ -phenyl	CH ₃	CH ₃	oil
	I-87	3-Cl-phenyl	CH ₃	CH ₃	97
	I-88	3-CH ₃ -phenyl	CH ₃	CH ₃	oil
	I-89	3-OH-phenyl	CH ₃	CH ₃	oil
30	I-90	4-Br-phenyl	CH ₃	CH ₃	102
	I-91	4-Cl-phenyl	CH ₃	CH ₃	76
	I-92	4-CN-phenyl	CH ₃	CH ₃	124
	I-93	4-OH-phenyl	CH ₃	CH ₃	145
35	I-94	4-Cl-phenyl	phenyl	COOCH ₃	147-154
	I-95	4-NO ₂ -phenyl	phenyl	COOCH ₃	163-171
	I-96	4-Br-phenyl	phenyl	CH ₃	162
	I-97	phenyl	phenyl	CH ₃	87-93
40	I-98	phenyl	tert-butyl	isopropyl	66-74
	I-99	phenyl	tert-butyl	n-butyl	73-80
	I-100	phenyl	tert-butyl	tert-butyl	62-68
45	I-101	4-Cl-phenyl	3-pyridyl	CF ₃	oil
	I-102	3-NO ₂ -phenyl	4-Cl-phenyl	C ₂ H ₅	oil
	I-103	2-CH ₃ -phenyl	4-Cl-phenyl	CH ₃	oil
	I-104	4-Cl-phenyl	4-pyridyl	CF ₃	oil

	No.	B	R ¹	R ⁴	Phys. data (m.p. [°C])
	I-105	3-CH ₃ -phenyl	C ₂ F ₅	CF ₃	oil
5	I-106	4-Cl-phenyl	C ₂ F ₅	CF ₃	103
	I-107	4-CN-phenyl	C ₂ F ₅	CF ₃	90
	I-108	4-CH ₃ -phenyl	C ₂ F ₅	CF ₃	99
	I-109	4-CH ₃ -phenyl	C ₂ F ₅	CF ₃	90
	I-110	4-OH-phenyl	C ₂ F ₅	CF ₃	oil
10	I-111	phenyl	C ₂ F ₅	CF ₃	70
	I-112	4-CH ₃ -phenyl	C ₂ F ₅	CH ₃	132
	I-113	4-NO ₂ -phenyl	C ₂ F ₅	CH ₃	78
	I-114	4-CF ₃ -phenyl	C ₂ F ₅	CH ₃	139
15	I-115	4-phenyl-phenyl	C ₂ F ₅	CH ₃	195
	I-116	3-F-phenyl	C ₂ F ₅	CH ₃	128
	I-117	3-F-phenyl	C ₂ F ₅	CH ₃	136
	I-118	4-Cl-phenyl	C ₂ F ₅	tert-butyl	91
20	I-119	4-CN-phenyl	C ₂ F ₅	tert-butyl	125
	I-120	4-OH-phenyl	C ₂ F ₅	tert-butyl	130
	I-121	phenyl	C ₂ F ₅	tert-butyl	92
	I-122	3,4-Cl ₂ -phenyl	C ₂ F ₅	tert-butyl	142
	I-123	4-CH ₃ -phenyl	C ₃ F ₇	2-thienyl	oil
25	I-124	4-Cl-phenyl	C ₃ F ₇	CF ₃	129
	I-125	4-CN-phenyl	C ₃ F ₇	CF ₃	123
	I-126	4-CH ₃ -phenyl	C ₃ F ₇	CF ₃	178
	I-127	4-NO ₂ -phenyl	C ₃ F ₇	CF ₃	130
30	I-128	4-OH-phenyl	C ₃ F ₇	CF ₃	111
	I-129	phenyl	C ₃ F ₇	CF ₃	103
	I-130	3,4-Cl ₂ -phenyl	C ₃ F ₇	CF ₃	oil
	I-131	3,4-Cl ₂ -phenyl	C ₃ F ₇	CF ₃	oil
35	I-132	4-F-phenyl	C ₃ F ₇	CH ₃	158
	I-133	3,4-Cl ₂ -phenyl	CF	tert-butyl	146
	I-134	3-CH ₃ -phenyl	CF ₃	2-furyl	oil
	I-135	4-Cl-phenyl	CF ₃	2-furyl	119
	I-136	4-CN-phenyl	CF ₃	2-furyl	133
40	I-137	4-CH ₃ -phenyl	CF ₃	2-furyl	94
	I-138	4-OH-phenyl	CF ₃	2-furyl	239
	I-139	4-Cl-phenyl	CF ₃	2-thienyl	160
	I-140	4-CH ₃ -phenyl	CF ₃	2-thienyl	oil
45	I-141	phenyl	CF ₃	3-pyridyl	oil
	I-142	3-Cl-phenyl	CF ₃	4-Cl-phenyl	oil

No.	B	R ¹	R ⁴	Phys. data (m.p. [°C])
5	I-143 2-OH-phenyl	CF ₃	C ₂ H ₅	oil
	I-144 4-OH-phenyl	CF ₃	C ₂ H ₅	oil
	I-145 4-Cl-phenyl	CF ₃	C ₂ H ₅	86
	I-146 3-CH ₃ -phenyl	CF ₃	C ₂ H ₅	oil
	I-147 4-CN-phenyl	CF ₃	C ₂ H ₅	101
10	I-148 4-CH ₃ -phenyl	CF ₃	C ₂ H ₅	84
	I-149 4-Br-phenyl	CF ₃	C ₂ H ₅	104
	I-150 phenyl	CF ₃	C ₂ H ₅	oil
	I-151 3,4-Cl ₂ -phenyl	CF ₃	C ₂ H ₅	85
	I-152 4-Cl-phenyl	CF ₃	i-C ₃ H ₇	92
15	I-153 4-CN-phenyl	CF ₃	i-C ₃ H ₇	182
	I-154 4-CH ₃ -phenyl	CF ₃	i-C ₃ H ₇	89
	I-155 4-OH-phenyl	CF ₃	i-C ₃ H ₇	103
	I-156 phenyl	CF ₃	i-C ₃ H ₇	48
	I-157 3,4-Cl ₂ -phenyl	CF ₃	i-C ₃ H ₇	87
20	I-158 3-F-phenyl	CF ₃	CH ₃	81
	I-159 4-CN-phenyl	CF ₃	tert-butyl	150
	I-160 4-Cl-phenyl	CF ₃	tert-butyl	132
	I-161 4-CH ₃ -phenyl	CF ₃	tert-butyl	86
	I-162 4-OH-phenyl	CF ₃	tert-butyl	205
25	I-163 phenyl	CF ₃	tert-butyl	62
	I-164 4-OH-phenyl	CH ₃	CH ₃	145
	I-165 4-phenyl-phenyl	tBu	CO ₂ CH ₃	oil

30

Table II



IB.1'

35

No.	B	R ¹	R ⁴	Phys. data (m.p. [°C])
40	II-1 phenyl	CF ₃	CH ₃	88
	II-2 4-CH ₃ -phenyl	CF ₃	CH ₃	104
	II-3 4-CH ₃ -phenyl	C ₂ F ₅	CH ₃	106
	II-4 4-Cl-phenyl	C ₂ F ₅	CH ₃	115
45	II-5 4-Br-phenyl	C ₂ F ₅	CH ₃	134
	II-6 4-NO ₂ -phenyl	C ₂ F ₅	CH ₃	155
	II-7 4-I-phenyl	C ₂ F ₅	CH ₃	149

No.	B	R ¹	R ⁴	Phys. data (m.p. [°C])	
5	II-8	4-phenyl-phenyl	C ₂ F ₅	CH ₃	131
	II-9	4-CH ₃ O-phenyl	C ₂ F ₅	CH ₃	Ö1
	II-10	4-CF ₃ -phenyl	C ₂ F ₅	CH ₃	131
	II-11	3-F-phenyl	C ₂ F ₅	CH ₃	78
	II-12	4-F-phenyl	C ₂ F ₅	CH ₃	120
10	II-13	phenyl	C ₃ F ₇	CH ₃	120
	II-14	4-CH ₃ -phenyl	C ₃ F ₇	CH ₃	105
	II-15	4-Br-phenyl	C ₃ F ₇	CH ₃	127
	II-16	4-NO ₂ -phenyl	C ₃ F ₇	CH ₃	135
	II-17	4-I-phenyl	C ₃ F ₇	CH ₃	137
15	II-18	3,4-Cl ₂ -phenyl	C ₃ F ₇	CH ₃	213
	II-19	4-phenyl-phenyl	C ₃ F ₇	CH ₃	138
	II-20	4-CH ₃ O-phenyl	C ₃ F ₇	CH ₃	116
	II-21	4-CF ₃ -phenyl	C ₃ F ₇	CH ₃	129
	II-22	3-F-phenyl	C ₃ F ₇	CH ₃	104
20	II-23	4-F-phenyl	C ₃ F ₇	CH ₃	100
	II-24	4-Cl-phenyl	CF ₃	CH ₃	132
	II-25	4-Br-phenyl	CF ₃	CH ₃	157
	II-26	4-NO ₂ -phenyl	CF ₃	CH ₃	161
	II-27	4-I-phenyl	CF ₃	CH ₃	134
25	II-28	4-phenyl-phenyl	CF ₃	CH ₃	144
	II-29	3,4-Cl ₂ -phenyl	CF ₃	CH ₃	203
	II-30	4-CH ₃ O-phenyl	CF ₃	CH ₃	110
	II-31	4-CF ₃ -phenyl	CF ₃	CH ₃	167
	II-32	3-F-phenyl	CF ₃	CH ₃	104
30	II-33	4-F-phenyl	CF ₃	CH ₃	143

35 Examples of the activity against harmful fungi

The fungicidal activity of the compounds of the formula I was demonstrated by the following experiments:

- 40 The active compounds, separately or together, were formulated as a 10% emulsion in a mixture of 70% by weight of cyclohexanone, 20% by weight of Nekanil® LN (Lutensol® AP6, wetting agent having emulsifying and dispersing action based on ethoxylated alkylphenols) and 10% by weight of Wettol® EM (nonionic emulsifier based on ethoxylated castor oil) and diluted with
- 45 water to give the desired concentration.

Use Example 1 - Activity against *Phytophthora infestans* on tomatoes

- Leaves of potted plants of the cultivar "Große Fleischtomate" were sprayed to run-off with an aqueous suspension made with a stock solution of 10% of active compound, 63% of cyclohexanone and 27% of emulsifier. The next day, the leaves were infected with an aqueous zoospore suspension of *Phytophthora infestans*. The plants were subsequently placed in a water-vapor-saturated chamber at from 16 to 18°C. After 6 days, the tomato blight had developed on the untreated, but infected, control plants to such an extent that it was possible to evaluate the disease level visually in %.
- In this test, the plants which have been treated with 250 ppm of the active compounds I-1 to I-4, I-6, I-7, I-9 to I-11, I-13 to I-16, I-26 to I-35, I-53, I-59, I-60, I-63, I-68, I-72, I-74, I-94, I-95, I-97, I-112, I-113, I-117, I-124, I-127, I-134, I-164 and II-13 showed up to 20% infection, whereas the untreated plants were 100% infected.

Use Example 2 - Activity against *Plasmopara viticola*

- Leaves of potted vines of the cultivar "Müller-Thurgau" were sprayed to run-off with an aqueous formulation of active compound made with a stock solution of 10% of active compound, 63% of cyclohexanone and 27% of emulsifier. To be able to assess the long-term action of the substances, the plants were, after the spray coating had dried on, kept in a greenhouse for 7 days. Only then were the leaves inoculated with an aqueous zoospore suspension of *Plasmopara viticola*. The vines were then placed in a water-vapor-saturated chamber at 24°C for 48 hours and subsequently in a greenhouse at from 20 to 30°C for 5 days. After this time, the plants were once more placed in a humid chamber for 16 hours, to promote sporangiophore eruption. The extent of the infection on the underside of the leaves was then determined visually.

- In this test, the plants which had been treated with 250 ppm of the active compounds I-3, I-4, I-10, I-11, I-27, I-34, I-35, I-46, I-47, I-53, I-54, I-73, I-112, I-113, I-114, I-116, I-117, I-124 and I-127 showed no more than 30% infection, whereas untreated plants were infected by 90%.

- Use Example 3 - Activity against *Botrytis cinerea* on bell pepper leaves

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Bell pepper seedlings of the cultivar "Neusiedler Ideal Elite" which had 4 - 5 well-developed leaves were sprayed to run-off with an aqueous preparation of active compound made with a stock solution of 10% of active compound, 63% of cyclohexanone and 27% of emulsifier. The next day, the treated plants were inoculated with a spore suspension of *Botrytis cinerea*, containing 1.7×10^6 pores/ml in a 2% strength aqueous Biomalz solution. The test plants were then placed into a controlled-environment cabinet at 22 to 24°C and high atmospheric humidity. After 5 days, the extent of fungal disease on the leaves was determined visually in %.

In this test, the plants which had been treated with 250 ppm of the active compounds I-11, I-13, I-24, I-26, I-29, I-30, I-45, I-47, I-57 to I-61, I-63, I-64, I-68, I-70, I-71, I-74, I-80, I-94, I-112, I-114, I-127 and II-13 showed an infection of at most 20%, whereas the untreated plants were 100% infected.

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